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(54) **METHOD FOR PRE-SODIATION OF NEGATIVE ELECTRODE, PRE-SODIATED NEGATIVE ELECTRODE, AND LITHIUM SECONDARY BATTERY COMPRISING SAME**

(57) Disclosed is a method for pre-sodiation of a negative electrode, including the steps of: interposing a negative electrode between a sodium (Na) ion-supplying metal sheet and a separator to prepare a simple cell; dipping the simple cell in an electrolyte for pre-sodiation; and electrochemically charging the simple cell dipped in the electrolyte for pre-sodiation to carry out pre-sodiation of the negative electrode. Also disclosed are a pre-sodi-

ated negative electrode, including: a current collector; a negative electrode active material layer disposed on at least one surface of the current collector and including a negative electrode active material; and a coating layer formed on the surface of the negative electrode active material layer and including Na-carbonate and Na, and a lithium secondary battery including the pre-sodiated negative electrode.

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DescriptionTECHNICAL FIELD

[0001] The present disclosure relates to a method for pre-sodiation of a negative electrode, pre-sodiated negative electrode and a lithium secondary battery including the same. Particularly, the present disclosure relates to a method for pre-sodiation of a negative electrode for improving the initial efficiency of a lithium secondary battery, pre-sodiated negative electrode and a lithium secondary battery including the same.

[0002] The present application claims priority to Korean Patent Application No. 10-2019-0110928 filed on September 6, 2019 in the Republic of Korea, the disclosures of which are incorporated herein by reference.

BACKGROUND ART

[0003] Recently, energy storage technology has been given an increasing attention. Efforts into research and development of electrochemical devices have been actualized more and more, as the application of energy storage technology has been extended to energy for cellular phones, camcorders and notebook PC and even to energy for electric vehicles. In this context, electrochemical devices have been most spotlighted. Among such electrochemical devices, development of rechargeable secondary batteries has been focused. More recently, active studies have been conducted about designing a novel electrode and battery in order to improve the capacity density and specific energy in developing such batteries.

[0004] Among the commercially available secondary batteries, lithium secondary batteries developed in the early 1990's have been spotlighted, since they have a higher operating voltage, significantly higher energy density, longer cycle life and a lower self-discharge rate, as compared to conventional batteries, such as Ni-MH, Ni-Cd and sulfuric acid-lead batteries using an aqueous electrolyte.

[0005] Since the conventional lithium secondary batteries use a lithium-intercalated compound, such as LiCoO_2 or LiMn_2O_4 , as a positive electrode, such batteries have been manufactured by using a carbon electrode, to which lithium is not intercalated, as a negative electrode. In the case of a carbon electrode, a passivated coating film is formed on the surface thereof upon the initial charge, and the coating film interrupts insertion of an organic solvent into a gap between carbon lattice layers and inhibits decomposition of the organic solvent. In this manner, stabilization of a carbon structure and reversibility of a carbon electrode can be improved to allow use of the carbon electrode as a negative electrode for a lithium secondary battery.

[0006] However, since the formation of such a coating film is an irreversible reaction, lithium ions are consumed, resulting in a decrease in battery capacity undesirably. In addition, since the charge/discharge efficiency of the carbon electrode and positive electrode is not completely 100%, lithium ion consumption occurs, as the cycle number is increased, resulting in the problems of a decrease in electrode capacity and degradation of cycle life.

[0007] Many studies have been conducted to solve the above-mentioned problems, and it has been found that use of a pre-lithiated carbon electrode as a negative electrode can provide a high-capacity lithium secondary battery with no decrease in capacity, since the coating film formation occurring upon the initial charge is performed in advance. It has been also found that cycle life can be improved significantly, since such a pre-lithiated carbon electrode compensates for lithium ions consumed as the cycle number is increased.

[0008] Then, active studies have been conducted about pre-lithiation of a negative electrode, such as a carbon electrode. Typically, a method for lithiating a carbonaceous active material through a physicochemical process and manufacturing an electrode, and a method for electrochemically pre-lithiating a carbon electrode have been considered.

[0009] However, there is a need for a novel method substituting for the above-mentioned pre-lithiation methods, since lithium used for the pre-lithiation methods is expensive.

DISCLOSURETechnical Problem

[0010] The present disclosure is designed to solve the problems of the related art, and therefore the present disclosure is directed to providing a method for pre-sodiation of a negative electrode for improving the initial efficiency of a lithium secondary battery.

[0011] The present disclosure is also directed to providing a negative electrode obtained by the method for pre-sodiation of a negative electrode, and a lithium secondary battery including the same.

Technical Solution

[0012] In one aspect of the present disclosure, there is provided a method for pre-sodiation of a negative electrode according to any one of the following embodiments.

[0013] According to the first embodiment of the present disclosure, there is provided a method for pre-sodiation of a negative electrode, including the steps of:

interposing a negative electrode between a sodium (Na) ion-supplying metal sheet and a separator to prepare a simple cell;

dipping the simple cell in an electrolyte for pre-sodiation; and

electrochemically charging the simple cell dipped in the electrolyte for pre-sodiation to carry out pre-sodiation of the negative electrode.

[0014] According to the second embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in the first embodiment, wherein the electrolyte for pre-sodiation includes a sodium salt and a non-aqueous solvent.

[0015] According to the third embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in the second embodiment, wherein the sodium salt includes NaCl, NaBr, NaI, NaClO₄, NaBF₄, NaB₁₀Cl₁₀, NaPF₆, NaCF₃SO₃, NaCF₃CO₂, NaAsF₆, NaSbF₆, NaAlCl₄, CH₃SO₃Na, CF₃SO₃Na, (CF₃SO₂)₂NNa, sodium chloroborate, sodium lower aliphatic carboxylate, sodium tetraphenylborate, or a mixture of two or more of them.

[0016] According to the fourth embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in any one of the first to the third embodiments, wherein the electrochemical charging is carried out, while the simple cell is pressurized.

[0017] According to the fifth embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in any one of the first to the fourth embodiments, wherein the electrochemical charging is carried out to 3-50% of the charge capacity of the negative electrode (based on Na-ion charge capacity).

[0018] According to the sixth embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in any one of the first to the fifth embodiments, wherein the electrochemical charging is carried out to 10-20% of the charge capacity of the negative electrode (based on Na-ion charge capacity).

[0019] According to the seventh embodiment of the present disclosure, there is provided the method for pre-sodiation of a negative electrode as defined in any one of the first to the sixth embodiments, wherein the sodium ion-supplying metal sheet includes a metal selected from sodium, sodium alloys and mixtures thereof, alone, or includes a metal having a substrate attached to one surface thereof for supporting the metal.

[0020] In another aspect of the present disclosure, there is provided a pre-sodiated negative electrode according to any one of the following embodiments.

[0021] According to the eighth embodiment of the present disclosure, there is provided a pre-sodiated negative electrode obtained by the method as defined in any one of the first to the seventh embodiments.

[0022] According to the ninth embodiment of the present disclosure, there is provided a pre-sodiated negative electrode including: a current collector; a negative electrode active material layer disposed on at least one surface of the current collector and including a negative electrode active material; and a coating layer formed on the surface of the negative electrode active material layer and including Na-carbonate and Na.

[0023] In still another aspect of the present disclosure, there is also provided a lithium secondary battery according to the following embodiment.

[0024] According to the tenth embodiment of the present disclosure, there is provided a lithium secondary battery including the pre-sodiated negative electrode as defined in the eighth or the ninth embodiment.

Advantageous Effects

[0025] The method for pre-sodiation of a negative electrode using an electrochemical charging process according to an embodiment of the present disclosure includes a preliminary reaction with sodium (Na), while not using lithium applied to the conventional pre-lithiation, so that the efficiency of a lithium secondary battery may be improved.

[0026] In other words, according to an embodiment of the present disclosure, sodium ion cheaper than lithium is used to carry out pre-sodiation so that an irreversible side reaction may be performed preliminarily on the surface of a negative electrode. As a result, when a lithium secondary battery is manufactured by using the pre-sodiated negative electrode, it is possible to improve the initial efficiency of the battery during charging/discharging.

BEST MODE

[0027] Hereinafter, preferred embodiments of the present disclosure will be described in detail. Prior to the description, it should be understood that the terms used in the specification and the appended claims should not be construed as limited to general and dictionary meanings, but interpreted based on the meanings and concepts corresponding to technical aspects of the present disclosure on the basis of the principle that the inventor is allowed to define terms appropriately for the best explanation.

[0028] In one aspect of the present disclosure, there is provided a method for pre-sodiation of a negative electrode, including the steps of:

interposing a negative electrode between a sodium (Na) ion-supplying metal sheet and a separator to prepare a simple cell;
dipping the simple cell in an electrolyte for pre-sodiation; and
electrochemically charging the simple cell dipped in the electrolyte for pre-sodiation to carry out pre-sodiation of the negative electrode.

[0029] Hereinafter, each step will be explained in more detail.

[0030] First, a negative electrode is interposed between a sodium ion-supplying metal sheet, which is a metal sheet supplying sodium (Na) ions, and a separator to prepare a simple cell.

[0031] The sodium ion-supplying metal sheet functions as a source for supplying sodium ions doped to the negative electrode, and may include a sodium ion-containing material selected from sodium, sodium alloys and mixtures thereof. The sodium alloys may include Na-Pb, Na-K alloys, or the like.

[0032] The sodium ion-supplying metal sheet may include a metal selected from sodium, sodium alloys and mixtures thereof, alone, or may further include a metal having a substrate attached to one surface thereof for supporting the metal. The substrate may include stainless steel (SUS), aluminum, nickel, titanium, baked carbon, copper, or the like.

[0033] The sodium ion-supplying metal sheet may have a thickness of 15-300 μm , or 20-100 μm .

[0034] The separator is disposed on one surface of the metal opposite to the negative electrode. The separator may function to prevent the sodium ion-supplying metal sheet and the negative electrode from being in direct contact with each other. This is because direct contact between the sodium ion-supplying metal sheet and the negative electrode may cause a doping process (sodiation), thereby making it difficult to control the doping process and interrupting a homogeneous doping process on the negative electrode. In other words, the separator may function to stabilize the doping process of the negative electrode. Herein, the separator may be any separator used for a conventional secondary battery with no particular limitation.

[0035] According to an embodiment of the present disclosure, the negative electrode may include, as a negative electrode active material, a carbonaceous material, silicon-based material (e.g. silicon oxide of SiO_x ($0 < x < 2$)), Si, or the like.

[0036] The carbonaceous material may be at least one selected from the group consisting of crystalline artificial graphite, crystalline natural graphite, amorphous hard carbon, low-crystalline soft carbon, carbon black, acetylene black, Ketjen black, Super P, graphene, and fibrous carbon, and preferably may be crystalline artificial graphite and/or crystalline natural graphite.

[0037] Besides the above-mentioned materials, particular examples of the negative electrode active material include a metal composite oxide, such as $\text{Li}_x\text{Fe}_2\text{O}_3$ ($0 \leq x \leq 1$), Li_xWO_2 ($0 \leq x \leq 1$), $\text{Sn}_x\text{Me}_{1-x}\text{Me}'_y\text{O}_z$ (Me: Mn, Fe, Pb, Ge; Me': Al, B, P, Si, an element of Group 1, Group 2 or Group 3 in the Periodic Table, or halogen; $0 < x \leq 1$; $1 \leq y \leq 3$; $1 \leq z \leq 8$), or the like; lithium metal; lithium alloy; silicon-based alloy; tin-based alloy; metal oxide, such as SnO, SnO_2 , PbO, PbO_2 , Pb_2O_3 , Pb_3O_4 , Sb_2O_3 , Sb_2O_4 , Sb_2O_5 , GeO, GeO₂, Bi_2O_3 , Bi_2O_4 , Bi_2O_5 , or the like; a conductive polymer, such as polyacetylene; a Li-Co-Ni type material; titanium oxide; lithium titanium oxide, or the like. Particularly, the negative electrode active material may include a carbonaceous material and/or Si.

[0038] In general, the negative electrode is obtained by applying negative electrode slurry prepared by dispersing a negative electrode active material, conductive material and a binder in a dispersion medium to a negative electrode current collector, and carrying out drying. If necessary, the electrode slurry may further include a filler.

[0039] The negative electrode current collector generally has a thickness of 3-500 μm . The negative electrode current collector is not particularly limited, as long as it has conductivity, while not causing any chemical change in the corresponding battery. Particular examples of the negative electrode current collector include copper, stainless steel, aluminum, nickel, titanium, baked carbon, copper or stainless steel surface-treated with carbon, nickel, titanium, silver, etc., aluminum-cadmium alloy, or the like. In addition, similarly to the positive electrode current collector, fine surface irregularities may be formed on the surface of the negative electrode current collector to reinforce the binding force to the negative electrode active material. The negative electrode current collector may be used in various shapes, including a film, sheet, foil, net, porous body, foamed body, non-woven web, or the like.

[0040] The conductive material is added generally in an amount of 1-50 wt% based on the total weight of the mixture including the negative electrode active material. Such a conductive material is not particularly limited, as long as it has conductivity, while not causing any chemical change in the corresponding battery. Particular examples of the conductive material include: graphite, such as natural graphite or artificial graphite; carbon black, such as carbon black, acetylene black, Ketjen black, channel black, furnace black, lamp black or thermal black; conductive fibers, such as carbon fibers or metallic fibers; metal powder, such as fluorocarbon, aluminum or nickel powder; conductive whiskers, such as zinc oxide or potassium titanate; conductive metal oxides, such as titanium oxide; conductive materials, such as a polyphenylene derivative; or the like.

[0041] Meanwhile, a graphitic material having elasticity may be used as a conductive material, optionally in combination with the above-mentioned materials.

[0042] The binder is an ingredient which assists binding of the active material with the conductive material and binding to the current collector, and is added generally in an amount of 1-50 wt%, based on the total weight of the mixture including the negative electrode active material. Particular examples of the binder include polyvinylidene fluoride, polyvinyl alcohol, carboxymethyl cellulose (CMC), starch, hydroxypropyl cellulose, regenerated cellulose, polyvinyl pyrrolidone, tetrafluoroethylene, polyethylene, polypropylene, ethylene-propylene-diene terpolymer (EPDM), sulfonated EPDM, styrene butadiene rubber (SBR), fluororubber, various copolymers, or the like.

[0043] The dispersion medium may include water, alcohols, such as ethanol, acetone, or the like.

[0044] The filler is an ingredient which inhibits swelling of the negative electrode and is used optionally. Such a filler is not particularly limited, as long as it is a fibrous material, while not causing any chemical change in the corresponding battery. Particular examples of the filler include: olefinic polymers, such as polyethylene or polypropylene; and fibrous materials, such as glass fibers or carbon fibers.

[0045] The negative electrode is allowed to face the sodium ion-supplying metal sheet with the separator interposed therebetween, thereby preparing a simple cell. Herein, the negative electrode may be prepared by cutting the negative electrode in such a manner that it may be provided with a non-coated tab portion and a negative electrode material-retaining portion.

[0046] According to an embodiment of the present disclosure, pre-sodiation is carried out in an electrolyte for pre-sodiation. To carry out pre-sodiation, the separator and the sodium ion-supplying metal sheet are stacked successively on the negative electrode active material layer of the negative electrode, and then a simple cell may be prepared, after jigs (e.g. planar jigs) are disposed above and below the negative electrode and the sodium ion-supplying metal sheet.

[0047] Next, the simple cell is dipped in the electrolyte for pre-sodiation.

[0048] The electrolyte for pre-sodiation may include a sodium salt and a non-aqueous solvent.

[0049] The sodium salt may include NaCl, NaBr, NaI, NaClO₄, NaBF₄, NaB₁₀Cl₁₀, NaPF₆, NaCF₃SO₃, NaCF₃CO₂, NaAsF₆, NaSbF₆, NaAlCl₄, CH₃SO₃Na, CF₃SO₃Na, (CF₃SO₂)₂NNa, sodium chloroborate, sodium lower aliphatic carboxylate, sodium tetraphenylborate, or a mixture of two or more of them.

[0050] The non-aqueous solvent may be any organic solvent used conventionally in the art with no particular limitation. Preferably, a high-boiling point organic solvent may be used so as to minimize consumption of the electrolyte for pre-sodiation, caused by evaporation during the pre-sodiation.

[0051] The non-aqueous solvent may include a carbonate solvent, ester solvent, or a mixture of two or more of them. Particular examples of the non-aqueous solvent include, but are not limited to: propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), dipropyl carbonate (DPC), dimethyl sulfoxide, acetonitrile, dimethoxyethane, diethoxyethane, tetrahydrofuran, N-methyl-2-pyrrolidone (NMP), ethyl methyl carbonate (EMC), gamma-butyrolactone, ethyl propionate, and methyl propionate, and such solvents may be used alone or in combination.

[0052] The electrolyte for pre-sodiation may further include an additive.

[0053] The additive may include vinylene carbonate, vinyl ethylene carbonate, fluoroethylene carbonate, salicylic acid, LiBF₄, lithium bis(trifluoromethanesulfonyl)imide (LITFSI), lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalate)borate (LiODFB), or a mixture of two or more of them.

[0054] According to an embodiment of the present disclosure, the simple cell may be dipped in the electrolyte for pre-sodiation for 1-30 hours so that the negative electrode may be wetted with the electrolyte for pre-sodiation. When the dipping time satisfies the above-defined range, the negative electrode active material may be wetted sufficiently with the electrolyte for pre-sodiation, thereby facilitating the subsequent process, pre-sodiation. In addition, it is possible to prevent the problem caused by an excessively long dipping time, the problem including degradation of the durability of the electrode and easy detachment of the active material from the current collector during processing. When the electrolyte for pre-sodiation infiltrates homogeneously into the negative electrode through the wetting, sodium ions isolated from the sodium ion-supplying metal sheet may be diffused homogeneously to the negative electrode, and thus pre-sodiation may be carried out with a homogeneous sodium ion concentration over the whole negative electrode.

[0055] To facilitate dipping/wetting of the simple cell in/with the electrolyte for pre-sodiation, the reactor for carrying out wetting may be converted into a vacuum state of less than 760 mmHg. Herein, the electrolyte for pre-sodiation with

which the simple cell is wetted may have a temperature of 30-60°C.

[0056] Then, the simple cell dipped in the electrolyte for pre-sodiation is charged electrochemically to carry out pre-sodiation of the negative electrode.

[0057] According to an embodiment of the present disclosure, the simple cell may be charged electrochemically by using a charger, after the simple cell is dipped in the electrolyte for pre-sodiation and even the inner part of the simple cell is wetted sufficiently with the electrolyte for pre-sodiation.

[0058] Herein, the extent of electric current during charging may be 0.1-10 mA/cm², 0.5-3 mA/cm², or 0.5-2 mA/cm². When the extent of electric current satisfies the above-defined range, there is an advantage in that sodium ions may react stably and homogeneously with the negative electrode.

[0059] According to an embodiment of the present disclosure, the electrochemical charging may be carried out to 3-50%, 5-30%, or 10-20% of the charge capacity of the negative electrode (based on Na-ion charge capacity). When the electrochemical charging is carried out within the above-defined range, it is possible to improve the initial efficiency and cycle characteristics of a battery. It is also possible to prevent the problem of degradation of stability caused by excessive electrodeposition of sodium. Herein, the charge capacity of the negative electrode may be determined from the theoretical capacity of the negative electrode active material loaded on the negative electrode, and the electrochemical charging may be carried out in such a manner that the charger may stop charging, after the simple cell is charged to a predetermined percentage (%) of capacity calculated within the above-defined range.

[0060] In addition, the electrochemical charging may be carried out, while the simple cell is pressurized.

[0061] The method for pressurizing the simple cell may be any method known to those skilled in the art with no particular limitation. For example, as a pressurizing member for the simple cell, a system configured to change the interval between a pair of planar jigs by using a device may be used.

[0062] The pressurizing member, such as jigs, may be made of a material having no reactivity with an organic electrolyte, and particular examples of the material include polyetheretherketone (PEEK).

[0063] According to an embodiment of the present disclosure, the pressurizing member may be mounted to the simple cell, after the simple cell is dipped in and wetted with the electrolyte for pre-sodiation. In a variant, the pressurizing member may be mounted to the simple cell in advance, before the simple cell is dipped in the electrolyte for pre-sodiation, and then the resultant structure may be dipped in the electrolyte for pre-sodiation so that the simple cell may be wetted with the electrolyte for pre-sodiation.

[0064] Particularly, when the simple cell is prepared by stacking the separator and the sodium ion-supplying metal sheet successively on the negative electrode active material layer of the negative electrode, and disposing jigs above and below the negative electrode and the sodium ion-supplying metal sheet, the simple cell provided with the jigs may be dipped in the electrolyte for pre-sodiation, and then electrochemical charging may be carried out, while the simple cell is pressurized with the jigs.

[0065] In a variant, the simple cell not provided with jigs may be dipped in the electrolyte for pre-sodiation, and then jigs may be mounted to the simple cell and electrochemical charging may be carried out, while the simple cell is pressurized with the jigs.

[0066] When applying a predetermined pressure by using a pressurizing member, such as jigs, electrochemical charging may be carried out, while the sodium ion-supplying metal sheet faces the negative electrode active material layer of the negative electrode with the separator interposed therebetween. The sodium ion-supplying metal sheet may be pressurized against the negative electrode active material layer by using the pressurizing member under a pressure of 10-3,000 kPa, 50-2,000 kPa, or 100-1,000 kPa. When the pressure satisfies the above-defined range, pre-sodiation may be carried out smoothly and the electrode may be prevented from being damaged physically.

[0067] When the simple cell is electrochemically charged under pressurization, it can be charged more homogeneously and stably, as compared to charging in a non-pressurized state.

[0068] Then, the negative electrode may be taken out of the electrolyte for pre-sodiation, washed with an organic solvent, and then dried. The organic solvent used for washing may include dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, or the like. In this manner, it is possible to dissolve sodium salt sufficiently and to wash the negative electrode, while causing no damage upon the negative electrode.

[0069] The drying may be carried out by the method generally known to those skilled in the art. For example, the negative electrode may be dried in a dry room at 20-40°C for 10 minutes to 5 hours.

[0070] In another aspect of the present disclosure, there is provided a pre-sodiated negative electrode obtained by the above-described method for pre-sodiation.

[0071] In addition, the pre-sodiated negative electrode according to an embodiment of the present disclosure includes: a current collector; a negative electrode active material layer disposed on at least one surface of the current collector and including a negative electrode active material layer; and a coating layer including Na-carbonate and Na and formed on the surface of the negative electrode active material layer.

[0072] The negative electrode is provided with a coating layer including Na-carbonate and Na and formed on the surface of the negative electrode active material layer. The coating layer corresponds to a passivated film formed by

the above-described pre-sodiation. In addition, since even the inner part of the negative electrode is wetted sufficiently with the electrolyte, the coating layer including Na-carbonate and Na may be formed not only on the surface of the negative electrode active material layer but also in the internal pores of the negative electrode active material layer.

[0073] During the pre-sodiation of the negative electrode, the electrolyte for pre-sodiation is in contact with the negative electrode active material to cause oxidative-reductive decomposition of the ingredients of electrolyte at the interface, and the decomposition products may be deposited or adsorbed on the interface to form a coating layer as a new interfacial layer.

[0074] The coating layer may include Na reduced and deposited after sodium ions migrate toward the negative electrode during the pre-sodiation, and Na-carbonate (Na_2CO_3) produced by the reductive decomposition reaction between sodium ions and a carbonate compound as an organic solvent. In addition to Na-carbonate and Na, the coating layer may further include $(\text{CH}_2\text{OCO}_2\text{Na})_2$, $(\text{CH}_2\text{CH}_2\text{OCO}_2\text{Na})_2$, $\text{NaO}(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_2\text{OCO}_2\text{Na}$, or the like.

[0075] The coating layer interrupts insertion of the organic solvent into the negative electrode active material layer to inhibit decomposition of the organic solvent, thereby improving stabilization of the negative electrode active material structure and negative electrode reversibility. In other words, the reaction of forming the coating layer is a preliminary reaction of the irreversible region of the negative electrode active material. Thus, it is possible to prevent the problems of consumption of lithium ions during the subsequent battery operation and degradation of battery capacity, thereby improving cycle life.

[0076] In still another aspect of the present disclosure, there is provided a lithium secondary battery including the above-described pre-sodiated negative electrode. In other words, an electrode assembly may be formed by using a positive electrode including a positive electrode active material, a separator and the pre-sodiated negative electrode, and the electrode assembly and an electrolyte may be introduced to a battery casing to provide a lithium secondary battery.

[0077] Particular examples of the positive electrode active material may include, but are not limited to: layered compounds such as lithium cobalt oxide (LiCoO_2) and lithium nickel oxide (LiNiO_2), or those compounds substituted with one or more transition metals; lithium manganese oxides such as those represented by the chemical formula of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ (wherein x is 0-0.33), LiMnO_3 , LiMn_2O_3 and LiMnO_2 ; lithium copper oxide (Li_2CuO_2); vanadium oxides such as LiV_3O_8 , LiV_3O_4 , V_2O_5 or $\text{Cu}_2\text{V}_2\text{O}_7$; lithium nickel oxides represented by the chemical formula of $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ (wherein M is Co, Mn, Al, Cu, Fe, Mg, B or Ga, and y is 0.01-0.3); ternary lithium manganese composite oxides represented by the chemical formula of $\text{LiMn}_{2-y}\text{M}_y\text{O}_2$ (wherein $M = \text{Co, Ni, Fe, Cr, Zn or Ta}$, and $y = 0.01-0.1$), or $\text{Li}_2\text{Mn}_3\text{MO}_8$ (wherein $M = \text{Fe, Co, Ni, Cu or Zn}$); LiMn_2O_4 in which Li is partially substituted with an alkaline earth metal ion; disulfide compounds; and $\text{Fe}_2(\text{MoO}_4)_3$; ternary lithium transition metal composite oxides, such as $\text{Li}(\text{Ni}_a\text{Co}_b\text{Mn}_c)\text{O}_2$ ($0 < a < 1$, $0 < b < 1$, $0 < c < 1$, $a + b + c = 1$); or the like.

[0078] The positive electrode active material may be dispersed in a solvent together with a binder polymer, conductive material and other additives to form positive electrode mixture slurry. Then, the positive electrode mixture slurry may be coated on at least one surface of a positive electrode current collector, followed by drying and pressing, to form a positive electrode.

[0079] Non-limiting examples of the positive electrode current collector include foil made of aluminum, nickel or a combination thereof, or the like, and non-limiting examples of the negative electrode current collector include foil made of copper, gold, nickel, copper alloy or a combination thereof, or the like.

[0080] The binder polymer, conductive material and other additives used in the positive electrode may be the same as or different from those used in the negative electrode. Reference will be made to the above description about the binder polymer and conductive material.

[0081] The separator is interposed between the positive electrode and the negative electrode, and an insulating thin film having high ion permeability and mechanical strength is used as the separator. The separator generally has a pore diameter of 0.01-10 μm and a thickness of 5-300 μm . The separator may include a porous polymer substrate, such as a porous polymer film substrate or porous polymer non-woven web substrate, alone, or may further include a porous coating layer disposed on at least one surface of the porous polymer substrate and containing inorganic particles and a binder polymer. The porous polymer film substrate may be a porous polymer film made of polyolefin, such as polyethylene or polypropylene. In addition to polyolefin, the porous polymer film substrate may be made of polyester, such as polyethylene terephthalate, polybutylene terephthalate or polyethylene naphthalene; polyacetal; polyamide; polycarbonate; polyimide; polyetherether ketone; polyether sulfone; polyphenylene oxide; polyphenylene sulfide; or the like, alone or in combination.

[0082] Non-limiting examples of the binder polymer include but are not limited to: polyvinylidene fluoride-co-hexafluoropropylene, polyvinylidene fluoride-co-trichloro ethylene, polymethyl methacrylate, polybutyl acrylate, polybutyl methacrylate, polyacrylonitrile, polyvinyl pyrrolidone, polyvinyl acetate, polyethylene-co-vinyl acetate, polyethylene oxide, polyarylate, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cyanoethyl pullulan, cyanoethyl polyvinylalcohol, cyanoethyl cellulose, cyanoethyl sucrose, pullulan, carboxymethyl cellulose, or the like.

[0083] According to an embodiment of the present disclosure, the binder polymer may be classified into a dispersant binder polymer also functioning as a dispersant, and a non-dispersant binder polymer. The dispersant binder polymer

is a polymer having at least one dispersion-contributing functional group in the backbone or sidechain of the polymer, and the dispersion-contributing functional group includes an OH group, CN group, or the like. Particular examples of the dispersant binder polymer include cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cyanoethyl pullulan, cyanoethyl polyvinyl alcohol, cyanoethyl cellulose, cyanoethyl sucrose, pullulan, carboxymethyl cellulose, or the like. Particular examples of the non-dispersant binder polymer include the above-listed binder polymers, except the examples of the dispersant binder polymer.

[0084] For example, the weight ratio of the inorganic particles to the total weight of the binder polymer and crosslinked polymer may be 50:50-99:1, particularly 70:30-95:5. When the weight ratio of the inorganic particles to the total weight of the binder polymer and crosslinked polymer satisfies the above-defined range, it is possible to prevent the problem of a decrease in pore size and porosity of the resultant coating layer, caused by an increase in content of the binder polymer and the crosslinked polymer. It is also possible to solve the problem of degradation of peeling resistance of the resultant coating layer, caused by a decrease in content of the binder polymer and the crosslinked polymer.

[0085] Non-limiting examples of the inorganic particles include inorganic particles having a dielectric constant of 5 or more, particularly 10 or more, inorganic particles having lithium ion transportability, or a mixture thereof.

[0086] Non-limiting examples of the inorganic particles having a dielectric constant of 5 or more may include BaTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), $\text{Pb}_{1-x}\text{La}_x\text{Zr}_{1-y}\text{Ti}_y\text{O}_3$ (PLZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{PbTiO}_3$ (PMN-PT), hafnia (HfO_2), SrTiO_3 , SnO_2 , CeO_2 , MgO , NiO , CaO , ZnO , ZrO_2 , Y_2O_3 , Al_2O_3 , SiC , $\text{AlO}(\text{OH})$, $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, or a mixture thereof.

[0087] As used herein, the term 'inorganic particles having lithium ion transportability' refers to inorganic particles which contain lithium elements and do not store lithium but transport lithium ions. Non-limiting examples of the inorganic particles having lithium ion transportability may include lithium phosphate (Li_3PO_4), lithium titanium phosphate ($\text{Li}_x\text{Ti}_y(\text{PO}_4)_3$, $0 < x < 2$, $0 < y < 3$), lithium aluminum titanium phosphate ($\text{Li}_x\text{Al}_y\text{Ti}_z(\text{PO}_4)_3$, $0 < x < 2$, $0 < y < 1$, $0 < z < 3$), (LiAlTiP) $_x\text{O}_y$ -based glass ($1 < x < 4$, $0 < y < 13$), such as $14\text{Li}_2\text{O}-9\text{Al}_2\text{O}_3-38\text{TiO}_2-39\text{P}_2\text{O}_5$, lithium lanthanum titanate ($\text{Li}_x\text{La}_y\text{TiO}_3$, $0 < x < 2$, $0 < y < 3$), lithium germanium thiophosphate ($\text{Li}_x\text{Ge}_y\text{P}_z\text{S}_w$, $0 < x < 4$, $0 < y < 1$, $0 < z < 1$, $0 < w < 5$), such as $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$, lithium nitride (Li_xN_y , $0 < x < 4$, $0 < y < 2$), such as Li_3N , SiS_2 -based glass ($\text{Li}_x\text{Si}_y\text{S}_z$, $0 < x < 3$, $0 < y < 2$, $0 < z < 4$), such as $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$, and P_2S_5 -based glass ($\text{Li}_x\text{P}_y\text{S}_z$, $0 < x < 3$, $0 < y < 3$, $0 < z < 7$), such as $\text{LiI-Li}_2\text{S-P}_2\text{S}_5$, or a mixture thereof.

[0088] Although there is no particular limitation in the thickness of the porous coating layer, it may be 1-10 μm , or 1.5-6 μm . Also, the porosity of the porous coating layer is not particularly limited, but it may be preferably 35-65%.

[0089] The electrolyte includes conventional electrolyte ingredients, such as an organic solvent and an electrolyte salt. The electrolyte salt that may be used is a salt having a structure of A^+B^- , wherein A^+ includes an alkali metal cation such as Li^+ , Na^+ , K^+ or a mixture thereof, and B^- includes an anion such as PF_6^- , BF_4^- , Cl^- , Br^- , I^- , ClO_4^- , AsF_6^- , CH_3CO_2^- , CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, $\text{C}(\text{CF}_3\text{SO}_2)_3^-$ or a mixture thereof. Particularly, a lithium salt is preferred. For example, LiClO_4 , LiCF_3SO_3 , LiPF_6 , LiAsF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or a mixture thereof may be used.

[0090] The organic solvent used for the electrolyte may include a solvent generally known to those skilled in the art, such as a cyclic carbonate solvent containing a halogen substituent or not; a linear carbonate solvent; an ester solvent, nitrile solvent, phosphate solvent, or a mixture thereof. Particular examples of the solvent that may be used include propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), dipropyl carbonate (DPC), dimethyl sulfoxide, acetonitrile, dimethoxyethane, diethoxyethane, tetrahydrofuran, N-methyl-2-pyrrolidone (NMP), ethyl methyl carbonate (EMC), gamma-butyrolactone (GBL), fluoroethylene carbonate (FEC), methyl formate, ethyl formate, propyl formate, methyl acetate, ethyl acetate, propyl acetate, pentyl acetate, methyl propionate, ethyl propionate, propyl propionate, butyl propionate, or a mixture thereof.

[0091] Injection of the electrolyte may be carried out in an adequate step during the process for manufacturing a battery depending on the manufacturing process of a final product and properties required for a final product. In other words, injection of the electrolyte may be carried out before the assemblage of a battery or in the final step of the assemblage of a battery.

[0092] There is no particular limitation in the appearance or casing of the lithium secondary battery according to an embodiment of the present disclosure. For example, the lithium secondary battery may have a cylindrical shape using a can, prismatic shape, pouch-like shape or a coin-like shape.

[0093] In addition, the lithium secondary battery according to an embodiment of the present disclosure may include any conventional lithium secondary batteries, such as lithium metal secondary batteries, lithium ion secondary batteries, lithium polymer secondary batteries or lithium ion polymer secondary batteries.

[0094] Examples will be described more fully hereinafter so that the present disclosure can be understood with ease. The following examples may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth therein. Rather, these exemplary embodiments are provided so that the present disclosure will be thorough and complete, and will fully convey the scope of the present disclosure to those skilled in the art.

Example 1

<Manufacture of Negative Electrode>

[0095] First, 92 parts by weight of hard carbon as a negative electrode active material, 3 parts by weight of Denka black as a conductive material, 3.5 parts by weight of styrene butadiene rubber (SBR) as a binder and 1.5 parts by weight of carboxymethyl cellulose as a binder and thickener were added to water as a dispersion medium to prepare negative electrode slurry.

[0096] The negative electrode slurry was coated on one surface of a copper current collector having a thickness of 20 μm and dried at a temperature of 80°C. Then, the negative electrode mixture layer was pressed by using a roll press device to a porosity of 28% so that it might satisfy the target thickness. After that, the resultant structure was dried in a vacuum oven at 130°C for 8 hours to obtain a negative electrode.

<Pre-sodiation Based on Electrochemical Charging>

[0097] The negative electrode obtained as described above was cut by using a cutter capable of cutting the negative electrode in such a manner that the negative electrode active material-retaining portion alone, except the non-coated tab portion, might have a dimension of 34 mm x 50 mm. Next, the negative electrode was allowed to face a sodium metal/SUS plate (including a SUS plate attached to one surface of sodium metal) as a sodium ion-supplying metal sheet with a separator (polypropylene porous polymer film) interposed therebetween, thereby providing a simple cell. The simple cell including the negative electrode-separator-sodium metal/SUS plate stacked successively was wetted with an electrolyte for pre-sodiation, including 1 M NaClO_4 dissolved in a solvent including ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed at a volume ratio of 3:7, and 2 wt% of fluoroethylene carbonate (FEC) added thereto, at 25°C for 3 hours, and then charged electrochemically by using a charger, while being pressurized under a pressure of 1000 kPa through pressurization jigs. In this manner, pre-sodiation of the negative electrode was carried out. Herein, the electric current was set to an extent of 2 mA/cm^2 and the simple cell was charged electrochemically to 20% of the negative electrode charge capacity (based on Na-ion charge capacity). After completing the pre-sodiation, the negative electrode was washed with dimethyl carbonate (DMC) and dried at room temperature, thereby providing a pre-sodiated negative electrode.

<Manufacture of Lithium Secondary Battery>

[0098] The pre-sodiated negative electrode obtained as described above was cut into a coin cell size, a separator (polyolefin porous polymer film) was interposed between the negative electrode and lithium metal foil as a counter electrode, and then an electrolyte containing 1 M LiPF_6 dissolved in a solvent including ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed at a volume ratio of 3:7 was injected thereto, thereby providing a coin-type half-cell.

Example 2

[0099] A pre-sodiated negative electrode and a coin-type half-cell including the same were obtained in the same manner as Example 1, except that the simple cell was charged electrochemically to 15% of the negative electrode charge capacity (based on Na-ion charge capacity).

Example 3

[0100] A pre-sodiated negative electrode and a coin-type half-cell including the same were obtained in the same manner as Example 1, except that the simple cell was charged electrochemically to 10% of the negative electrode charge capacity (based on Na-ion charge capacity).

Comparative Example 1

[0101] A negative electrode and a coin-type half-cell including the same were obtained in the same manner as Example 1, except that no pre-sodiation was carried out.

Comparative Example 2

<Manufacture of Negative Electrode>

[0102] First, 92 parts by weight of hard carbon as a negative electrode active material, 3 parts by weight of Denka black as a conductive material, 3.5 parts by weight of styrene butadiene rubber (SBR) as a binder and 1.5 parts by weight of carboxymethyl cellulose as a binder and thickener were added to water as a dispersion medium to prepare negative electrode slurry.

[0103] The negative electrode slurry was coated on one surface of a copper current collector having a thickness of 20 μm and dried at a temperature of 80°C. Then, the negative electrode mixture layer was pressed by using a roll press device to a porosity of 28% so that it might satisfy the target thickness. After that, the resultant structure was dried in a vacuum oven at 130°C for 8 hours to obtain a negative electrode.

<Pre-sodiation>

[0104] First, Na-metal powder (50 μm) was applied to the negative electrode obtained as described above in an amount sufficient for carrying out electrochemical charging to 20% of the negative electrode charge capacity (based on Na-ion charge capacity), and then the resultant structure was allowed to stand in an electrolyte including 1 M NaClO_4 dissolved in a solvent including ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed at a volume ratio of 3:7, and 2 wt% of fluoroethylene carbonate (FEC) added thereto, for 3 hours to carry out pre-sodiation. Then, the negative electrode was washed with DMC and dried at room temperature, thereby providing a pre-sodiated negative electrode.

<Manufacture of Lithium Secondary Battery>

[0105] The pre-sodiated negative electrode obtained as described above was cut into a coin cell size, a separator (polyolefin porous polymer film) was interposed between the negative electrode and lithium metal foil as a counter electrode, and then an electrolyte containing 1 M LiPF_6 dissolved in a solvent including ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed at a volume ratio of 3:7 was injected thereto, thereby providing a coin-type half-cell.

<Initial Reversibility Test>

[0106] Each of the coin-type half-cells according to Examples 1-3 and Comparative Examples 1 and 2 was tested in terms of charge/discharge reversibility by using an electrochemical charger. During charging, electric current was applied at a current density of 0.1 C-rate to a voltage of 0.005 V (vs. Li/Li^+). During discharging, each half-cell was discharged at the same current density to a voltage of 1.5 V. Herein, the first cycle efficiency was determined as a ratio of discharge capacity/charge capacity. The results are shown in the following Table 1.

[Table 1]

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2
First cycle efficiency (%)	94	90	87	80	84

[0107] Referring to Table 1, in the case of Examples 1-3, the preliminary reaction in the irreversible region of hard carbon through pre-sodiation based on electrochemical charging provides an improved initial efficiency during charging/discharging of each lithium secondary battery. On the contrary, when carrying out no pre-sodiation in the case of Comparative Example 1, the lithium secondary battery shows a low initial efficiency. In addition, when carrying out pre-sodiation by loading sodium metal directly on the negative electrode in the case of Comparative Example 2, sodium metal is not used sufficiently for pre-sodiation but remains as it is, and thus the initial efficiency is not improved significantly.

[0108] The present disclosure has been described in detail. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the disclosure, are given by way of illustration only, since various changes and modifications within the scope of the disclosure will become apparent to those skilled in the art from this detailed description.

Claims

1. A method for pre-sodiation of a negative electrode, comprising the steps of:

interposing a negative electrode between a sodium (Na) ion-supplying metal sheet and a separator to prepare a simple cell;
 dipping the simple cell in an electrolyte for pre-sodiation; and
 electrochemically charging the simple cell dipped in the electrolyte for pre-sodiation to carry out pre-sodiation of the negative electrode.

2. The method for pre-sodiation of a negative electrode according to claim 1, wherein the electrolyte for pre-sodiation comprises a sodium salt and a non-aqueous solvent.
3. The method for pre-sodiation of a negative electrode according to claim 2, wherein the sodium salt comprises NaCl, NaBr, NaI, NaClO₄, NaBF₄, NaB₁₀Cl₁₀, NaPF₆, NaCF₃SO₃, NaCF₃CO₂, NaAsF₆, NaSbF₆, NaAlCl₄, CH₃SO₃Na, CF₃SO₃Na, (CF₃SO₂)₂NNa, sodium chloroborate, sodium lower aliphatic carboxylate, sodium tetraphenylborate, or a mixture of two or more of them.
4. The method for pre-sodiation of a negative electrode according to claim 1, wherein the electrochemical charging is carried out, while the simple cell is pressurized.
5. The method for pre-sodiation of a negative electrode according to claim 1, wherein the electrochemical charging is carried out to 3-50% of the charge capacity of the negative electrode (based on Na-ion charge capacity).
6. The method for pre-sodiation of a negative electrode according to claim 1, wherein the electrochemical charging is carried out to 10-20% of the charge capacity of the negative electrode (based on Na-ion charge capacity).
7. The method for pre-sodiation of a negative electrode according to claim 1, wherein the sodium ion-supplying metal sheet comprises a metal selected from sodium, sodium alloys and mixtures thereof, alone, or includes a metal having a substrate attached to one surface thereof for supporting the metal.
8. A pre-sodiated negative electrode obtained by the method as defined in any one of claims 1 to 7.
9. A pre-sodiated negative electrode comprising: a current collector; a negative electrode active material layer disposed on at least one surface of the current collector and comprising a negative electrode active material; and a coating layer formed on the surface of the negative electrode active material layer and comprising Na-carbonate and Na.
10. A lithium secondary battery comprising the pre-sodiated negative electrode as defined in claim 9.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER**H01M 4/139(2010.01)i; H01M 4/04(2006.01)i; H01M 4/13(2010.01)i; H01M 10/052(2010.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 4/139(2010.01); C01G 45/12(2006.01); C01G 51/00(2006.01); H01M 10/054(2010.01); H01M 10/0585(2010.01);
H01M 4/04(2006.01); H01M 4/131(2010.01); H01M 4/1391(2010.01); H01M 4/38(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & keywords: 이차전지 (secondary battery), 음극 (anode), 전소듦화 (presodiation), 분리막 (separator), 침지 (immerse), 전해액 (electrolyte)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

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“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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“P” document published prior to the international filing date but later than the priority date claimed

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“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

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